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H. W. HUNTLEY

THE ISOLATION AND IDENTIFICATION
OF SOME OF THE COMPOUNDS OF
COAL TAR CREOSOTE

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**THE ISOLATION AND IDENTIFICATION OF SOME OF
THE COMPOUNDS OF COAL TAR CREOSOTE**

BY

HOWARD WHITE HUNTLEY

**A THESIS SUBMITTED FOR THE DEGREE
OF MASTER OF ARTS**

UNIVERSITY OF WISCONSIN

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INTRODUCTION.

The distillate of coal tar known as creosote oil has been used for a long time as a preservative of timber against the attack of fungi and marine borers. The amount of coal tar creosote consumed in the United States in the past few years is shown by the following table:

.....					
. Total gallons		. Domestic		. Imported	
.Year .	creosote	
.	.	.Gallons .	Per cent..	Gallons .	Per cent..
.....					
1908	56000000	17360000	31	38640000	69
1909	51431212	13862171	27	37569041	73
1910	63266271	18184355	29	45081916	71
1911	73027335	21510629	29	51516706	71
1912	83666490	31135195	37	52531295	63
1913	108373359	41700167	38	66673192	62
.....					

In spite of the fact that such large quantities are used each year as a preservative of timber, there are no actual data as to what constitutes the toxic principle, although a number of hypotheses have been advanced.

Formerly it was supposed that oils high in tar acids or phenols were most desirable for this purpose. It has been shown that such oils are extremely volatile and are slightly soluble in water and disappear from the wood through leaching.

It was also claimed that oils high in naphthalene gave the best results, but these are found to be as inefficient as the light oils and for the same reason.

The latest hypotheses seem to lean more to the use of

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high boiling oils or those containing high boiling fractions, as the best preservatives of wood.

The Forest Products Laboratory of Madison Wisconsin, in an attempt to solve the problem in a commercial way, made arrangements with the tar distilling people so that they were able to obtain five fractions, which presumably had the following boiling points:

Fraction 1 was supposed to be an oil distilling up to 205°C . This oil included a large proportion of phenol, toluol, xylol, benzene, some naphthalene and higher boiling components.

Fraction 2 was supposed to be an oil distilling from 205 to 250°C . It contained chiefly naphthalene.

Fraction 3 was an oil boiling from 250 to 295°C ., and contained what is known as anthracene oil.

Fraction 4, boiling between 295 and 320°C ., was considered as the anthracene fraction.

Fraction 5 was the residue boiling above 320°C . This contained a large amount of anthracene solid as well as pitch and other materials.

Toxicity tests in petri dishes on these fractions gave the following results:

.....		
		Killing point.
Preservative	
		Fomes annosus
.....		
Coal tar creosote	Per cent.	Lbs per Cu. Ft.media
.....		
Fraction 1	0.30	0.187
Fraction 2	0.225	0.140
Fraction 3	0.325	0.203
Fraction 4	3.30	2.059
Fraction 5	33.00	20.59
.....		

These tests showed, as far as toxicity is concerned, that the low boiling fractions are most efficient. The service tests however, showed that fractions 4 and 5 preserved wood for a longer time than the lower fractions. In general, the higher boiling oils have a longer preserving action than the lower boiling oils, although their toxicity is considerably less.

On account of this contradictory test, it was thought that it would be of interest to isolate as many as possible of the compounds in fraction 4 and to determine what the toxicity of these compounds would be towards wood destroying fungi and if possible towards marine borers.

Purpose of this work.

The purpose of this work is, therefore, to isolate the various components of fraction 4 in as high degree of purity as possible and to test these compounds for their toxicity against fungi. Arrangements have also been made with Dr. L. F. Shackell, connected with the Bureau of Fisheries, Washington, D.C., to test

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out these same materials against marine borers.

Manner of conducting the work.

In order to be assured that the compounds isolated were actually present in coal tar creosote and had not been formed by chemical treatment of the oil, the first step in isolating the compounds was a very thorough fractionation. This fractionation was followed by crystallization, separating them by the use of inert solvents such as alcohol, ether, petroleum ether etc.

Wherever it was possible such solvents were used and in no case was the original oil treated with stronger agents until the greater part of the work was completed and they were used then because the material available had been reduced to a very small bulk and it was apparent that no other means of separation was possible for the quantities of material at hand. At the end of the separation by mechanical means, the residues left as oils, were treated in the following manner; A number of the fractions were combined and a portion of the combined oil was saved in its original condition. The remaining parts of the fractions were separated into tar acids, tar bases and neutral oils. Toxicity tests will be made on all four of these portions of the original oil. In addition to their toxicity, tests will be made on all the compounds separated in a state of purity.

Experimental part.

In view of the fact that mechanical separation is desired, rather than chemical, practically the only method available for separation into component parts, was fractional distillation.

Apparatus.

In the preliminary distillation, a flask of large capacity was used. As the research progressed, it was found necessary to vary the apparatus in regard to size and form. In general air condensers were used. The length of the condenser was varied to suit the conditions. A thermometer which had been carefully calibrated was used. The correction for emergent stem was made in all the distillations. This was necessary because the distance from the delivery tube of the flask to the top of the neck of different flasks varies, and in order to have comparable temperatures in the many distillations, this correction could not be neglected.

Fractionations.**Fractionation I.**

The first fractionation was made in a commercial still and was supposed to give a distillate ranging between 295 and 320°.

Fractionation II.

The first fractionation made in connection with this research, and which was really the second distillation of the oil, was made in a two liter Jena distilling flask. This fractionation was repeated until eight liters had been distilled. The sub-fractions were divided as follows:

1A.....	270 to 280°.
2A.....	280 to 290°.
3A.....	290 to 300°.
4A.....	300 to 310°.

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5A..... 310 to 320°.

6A..... 320 to 330°.

Physical condition of sub-fractions.

1A..... Brown oil

2A..... " " with small amount of solids.

3A..... " " " increase of solids.

4A..... " " " still further increase in solids

5A..... Semi-solid.

6A..... Apparently solid.

The solid material of the sub-fractions 4A and 5A was separated from the oil by filtration. Part of the solid material was refractionated. A Ladenburg flask was used for this distillation:

4A (Solid).

Temperature	Per cent.
Below 290°.....	8.30
290 to 300°.....	20.20
300 to 310°.....	26.18
310 to 320°.....	20.20
320 to 330°.....	17.88
330 to 340°.....	8.10

5A (Solid)

Below 300°.....	8.24
300 to 310°.....	25.32
310 to 320°.....	31.54
320 to 330°.....	18.41
330 to 340°.....	16.48

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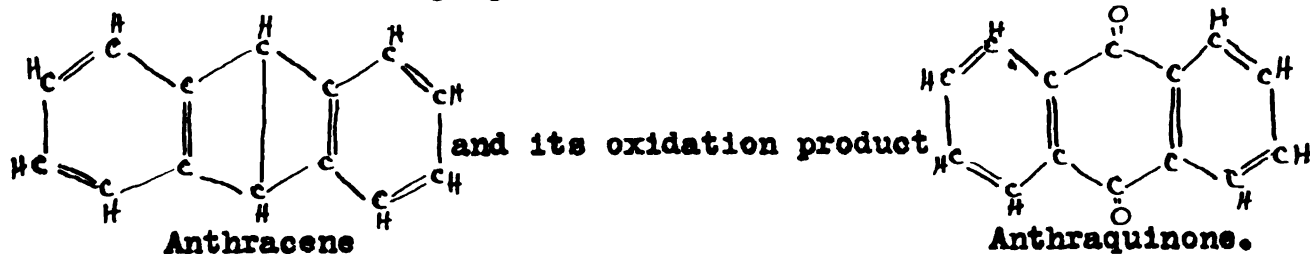
Fractional distillation of the solid material of the sub-fractions gave no satisfactory separation. The thermometer registered a gradual and uniform rise in temperature, indicating that the boiling points of the compounds present were so nearly identical or influenced each other to such an extent that a separation by fractional distillation under ordinary conditions would be impossible.

Crystallization.

3A (Solid).

Part of the solid material was crystallized from 95% alcohol until a constant melting point of the crystals was obtained.

Identification: The crystals came out in small scales or leaflets, nearly colorless, and melted at from 212 to 213°. The oxidation compound formed with chromic acid melted at from 278 to 280°. These properties correspond to those of



As a further proof of its identification, a few of the pure crystals were mixed with crystals known to be anthracene. The mixture melted at from 212 to 213°.

The alcoholic filtrate was partially evaporated and allowed to crystallize again. The crystals were separated by filtration. The filtrate was evaporated still further and allowed to crystallize. The melting points of the different crops of crystals obtained in this way varied from 104 to 111°.

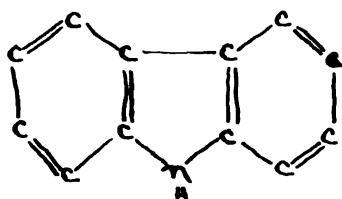
The picrate of these crystals melted at from 138 to 143°. This is very close to the melting point of the picrate of phenanthrene but the melting point of phenanthrene is 99°. The conclusion is that there are several hydrocarbons in the mixture.

A separation of the hydrocarbons in the above mixture was attempted by crystallization from dilute alcohol with the following results:

Percentage alcohol.	Melting point of crystals.
95.....	104 to 108°
90.....	104 to 110°
85.....	123 to 125°
80.....	120 to 123°
75.....	123 to 125°
70.....	121 to 125°
60.....	125 to 135°
50	
40	Below 100°.
30	

All the crystals melting between 104 and 135° were crystallized from petroleum ether.

Identification: The crystals from the petroleum ether were white scales or plates and melted at from 238 to 239°. The compound formed with picric acid melted at 183°. These melting points justify the conclusion that we are dealing with



Carbazol

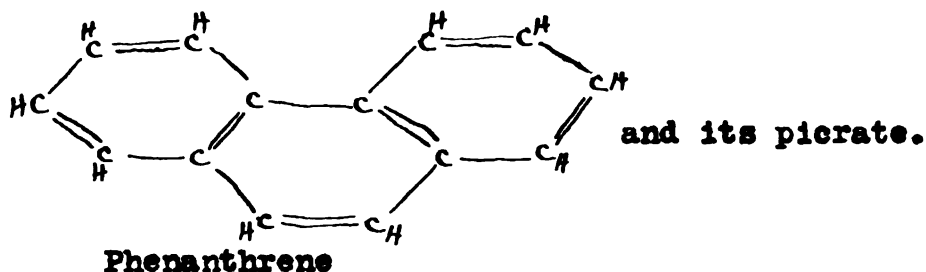
and its picrate.

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The petroleum ether solution was evaporated to dryness. It will be remembered that this residue is soluble in an excess of 95% alcohol since it was left in solution along with carbazol when anthracene was removed. A number of solvents, including benzene, acetone, ether and alcohol were used in attempt to further purify the petroleum ether residue. A 50 to 60% solution of alcohol proved to be the proper solvent.

Identification: Crystals melting between 98.5 and 99.4 were obtained. The compound formed with picric acid melted between 142 and 144°. These melting points correspond to those of



Part of the solid material of the sub-fractions 4A and 5A was subjected to the same crystallizations as sub-fraction 3A, with the exception that the alcoholic residue from the anthracene crystallization was crystallized immediately from petroleum ether instead of from dilute alcohol. In each sub-fraction, anthracene, carbazol, and phenanthrene were found. The solid material from sub-fractions 3A, 4A, 5A, and 6A was combined and later separated into its components.

A small portion of the combined solids was redistilled. There was a range from 295° to above 330°. The fraction coming over between 295° and 305° was crystallized from 95% alcohol. A small quantity of anthracene was obtained. The alcoholic solution was partially evaporated and allowed to crystallize. These crystals were again crystallized from 95% alcohol. The crystals

melted between 113 and 115°, and the picrate melted between 81° and 92°. These melting points correspond to those of fluorene and its picrate. Fluorene and phenanthrene have practically the same solubility in the different solvents. Hence, it would be difficult to separate them by crystallization. The wide range in the melting point of the picrate indicates a mixture.

We have disposed of the solid material obtained by fractionation II.

Fractionation III.

The oils of all the sub-fractions of fractionation II was the next material to receive attention. It was thought advisable to subject them to another distillation to determine if any further precipitation of solids would occur. In order to secure a more efficient separation, a Hempel flask and bead column was used in this fractionation. Ten degree fractions were taken. 1A (270-280°).

The oil from this fraction distilled from 210 to above 290°. Solid material separated in the ten degree fractions distilling from 210 to 230°. The remaining fractions were oils. 2A (280-290°).

The oil from this sub-fraction distilled from 230 to above 300°. Solid material precipitated in the fraction distilling between 290 and 300°. 3A (290-300°).

The oil distilled from 240 to above 320°. Solid material precipitated in the ten degree fractions distilling above 290°. 4A (300-310°).

This oil distilled from 254 to above 326°. Solids precipitated

100 100 100

ed in the fractions distilling above 290° .

5A ($310-320^{\circ}$).

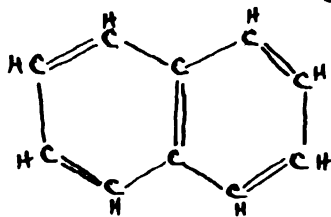
The oil of this sub-fraction distilled from 270° to above 330° . Solid material precipitated in all the ten degree fractions distilling above 290° .

6A ($320-330^{\circ}$).

The oil of this sub-fraction distilled between 278° and 330° . Solid material occurred in the fractions distilling above 290° .

The ten degree fractions having the same boiling points were combined. The solid material which had separated in certain fractions was removed from the oil by filtration. The solid material in the fractions distilling between 210° and 230° was crystallized from 95% alcohol.

Identification: The crystals were in the form of leaflets or plates and melted between 79° and 80° . The compound formed with picric acid melted between 150° and 151° . The odor of the crystals and the melting points correspond to



Naphthalene

and its picrate.

The solid material in the fractions distilling between 290° and 330° was separated from the oil by filtration. Anthracene, carbazol and phenanthrene were obtained by crystallization from the solvents previously employed..

Thus, it is seen that by fractionation III it was possible to isolate naphthalene.

Fractionation IV.

The oil of each ten degree fraction obtained in fractionation III was distilled into ten degree fractions. The solid material precipitating in these new fractions proved to be compounds similar to those obtained in the previous fractionation. No new compound was isolated. In this fractionation the lowest boiling oil distilled at 160° and the highest above 330° .

Fractionation V.

The oil of the ten degree fractions obtained in fractionation IV were again distilled into ten degree fractions. Very little solid material precipitated and only the compounds previously isolated were found. The range in temperature in this fractionation was from 137° to above 326° .

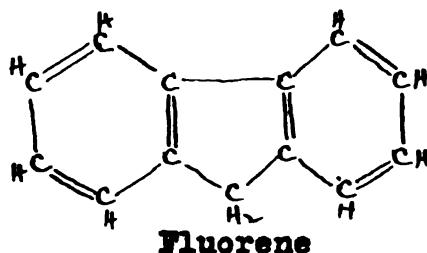
Fractionation VI.

It was noticed that in certain fractions in fractionation V, there was a tendency for the distillate to solidify in the delivery tube. After mixing with the other oils of that particular fraction, the solid material disappeared. This led to the belief that the fractions should be made in a smaller range of temperature. In this fractionation five degree fractions were made. This was impossible, however, in the fractions distilling below 200° because of the small quantities available. As a result of this fractionation, solids precipitated in the fractions distilling between 285° and 295° ; also quite an appreciable quantity precipitated from the fractions ^{distilling} between 215° and 230° .

The solids in the fraction distilling between 285° and 290° were separated from the oil by filtration, and washed with

alcohol while still on the filter. They were then crystallized from 95% alcohol.

Identification: The crystals formed in small plates and melted between 112° and 113° . The compound formed with picric acid melted between 78° and 79° . These melting points correspond to those of

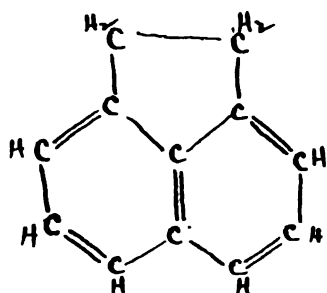


and its picrate.

The solids precipitating in the fractions distilling between 215° and 230° was naphthalene.

The five degree fractions distilling between 230° and 285° were allowed to stand for two weeks. No solid material precipitated. A flask containing a small quantity of oil distilling between 280° and 285° had been left unstoppered during the two weeks. A small quantity of water was introduced into the flask by mistake. After shaking the flask vigorously it was noticed that crystals began to form. The main body of the oil from this fraction was seeded with these crystals. A large quantity of crystals slowly formed. The crystals were separated from the oil by filtration and crystallized from 95% alcohol.

Identification: The pure product came out in long white needles which melted between 93.5° and 94.5° . The addition product formed with picric acid melted at 160° . These melting points correspond to those of

**Acenaphthene**

and its picrate.

A small portion of the oil from the five degree fractions distilling between 265° and 280° was cooled in an ice bath. By vigorously rubbing the walls of the containing vessel with a glass rod, crystals were formed. All of the oil of these fractions was brought to the temperature of melting ice. The crystals which had been obtained by rubbing the walls of the vessel were introduced into their corresponding fractions. Crystals formed in each fraction.

The crystals were separated from the oils by filtration. It was necessary to use a cold funnel and to filter while cold to prevent liquifaction of the crystals. These crystals were recrystallized from 95% alcohol. Acenaphthene was the only compound obtained. The oils from which acenaphthene had been removed were again refractionated into five degree fractions. Acenaphthene precipitated in the fractions distilling between 270° and 285° . The oil distilling above 285° yielded fluorene. Further refractionation of the oils remaining failed to produce any noticeable separation.

The following table will bring out the peculiarities in the boiling point of fraction 4 coal tar creosote encountered on repeated distillation:

.....		
Number of	Temperatures	
	
Fractionation	Highest	Lowest
.....		
I.....	320°	295°
II.....	330	270
III.....	330	210
IV.....	330	160
V.....	330	137
VI.....	326	137
.....		

The oils, from which solids would not precipitate after careful refractionation, distilled from 137° to 200° and from 233° to 270°.

The group of fractions distilling between 137° and 200° was combined. There was less than 25 c.c. of the oil. A rough test showed that the oil contained approximately 15% tar acids. The oil was set aside and its toxicity will be tested.

The group of fractions distilling between 233° and 270° was combined. There was between 125 and 150 c.c. of the oil. It was found to contain approximately 5% tar acids. It had a strong odor of tar bases. About 50 c.c. of the oil was set aside and its toxicity will be tested. The remaining portion is to be separated into tar acids, tar bases and neutral oils, and toxicity tests will be made on each.

CONCLUSIONS.

A study of the oil known as fraction 4 coal tar creosote, has

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shown that it is possible to isolate in a very high degree of purity at least six compounds without the use of chemical reagents. These compounds were anthracene, phenanthrene, acenaphthene, fluorene, naphthalene, and carbazol, the first five being hydrocarbons. The former three occur in about equal proportions and in much larger quantities than the latter three.

From a practical consideration, one of the most important results obtained from this work has been to direct attention to the presence of low boiling oils even in fractions boiling as high as 150° above the boiling point of these oils.

Preliminary tests show that these oils contain comparatively large amounts of tar acids as well as tar bases. It may be that the oils investigated owe their toxic effect to this small quantity of light oil, since it is known that tar acids, tar bases and also the xylols are very toxic.

Toxicity determinations will be made later.

ACCEPTED

S. F. Acree

Professor of Chemistry
of Forest Products.

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